



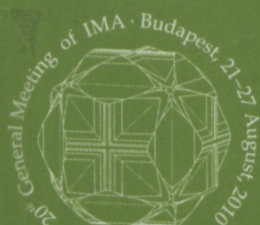
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BOGDAN P. ONAC & TUDOR TĂMAȘ

Cave minerals of west-central Romania

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HELYBEN
OLVASHATÓ

Cave minerals of west-central Romania

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1. The karst of the Pădurea Craiului Mountains – an overview

The Pădurea Craiului Mountains (“King Forest Mountains”), hereafter PCM, represents a clearly marked unit in the northern part of the Apuseni Mountains. One may summarise their setting as a Mesozoic peninsula bordered by Neogene basins. From a geomorphological point of view it is a fragmented platform, with a series of summits and isolated massifs of which elevation decreases continuously from SE to NW (from 1027 to 350 m).

The PCM lie in northwestern Romania. As part of the Apuseni Mountains, they cover approximately 750 km², extending westward towards Oradea (Fig. 1). To the north and

to the south, they are bounded by the Neogene Vad-Borod and Beiuş basins, respectively. In the east, they border the volcanic Vlădeasa massif, with the Iadei Valley (graben structure) acting as a demarcation line between the two massifs.

The PCM are formed mainly of deposits belonging to the *Bihor Unit* and *Apusenides* (Balintoni, 1997). The sedimentary formations of the *Bihor Unit* trace out a vast monocline. To the east and southeast, the monocline exposes a crystalline basement, covered towards the northwest by progressively younger formations (the Early Cretaceous deposits near Oradea being the youngest). Within the sedimentary succession of the *Bihor Unit* there are three thick carbonate sequences of special karstological importance (Ivanovici *et al.*, 1976):

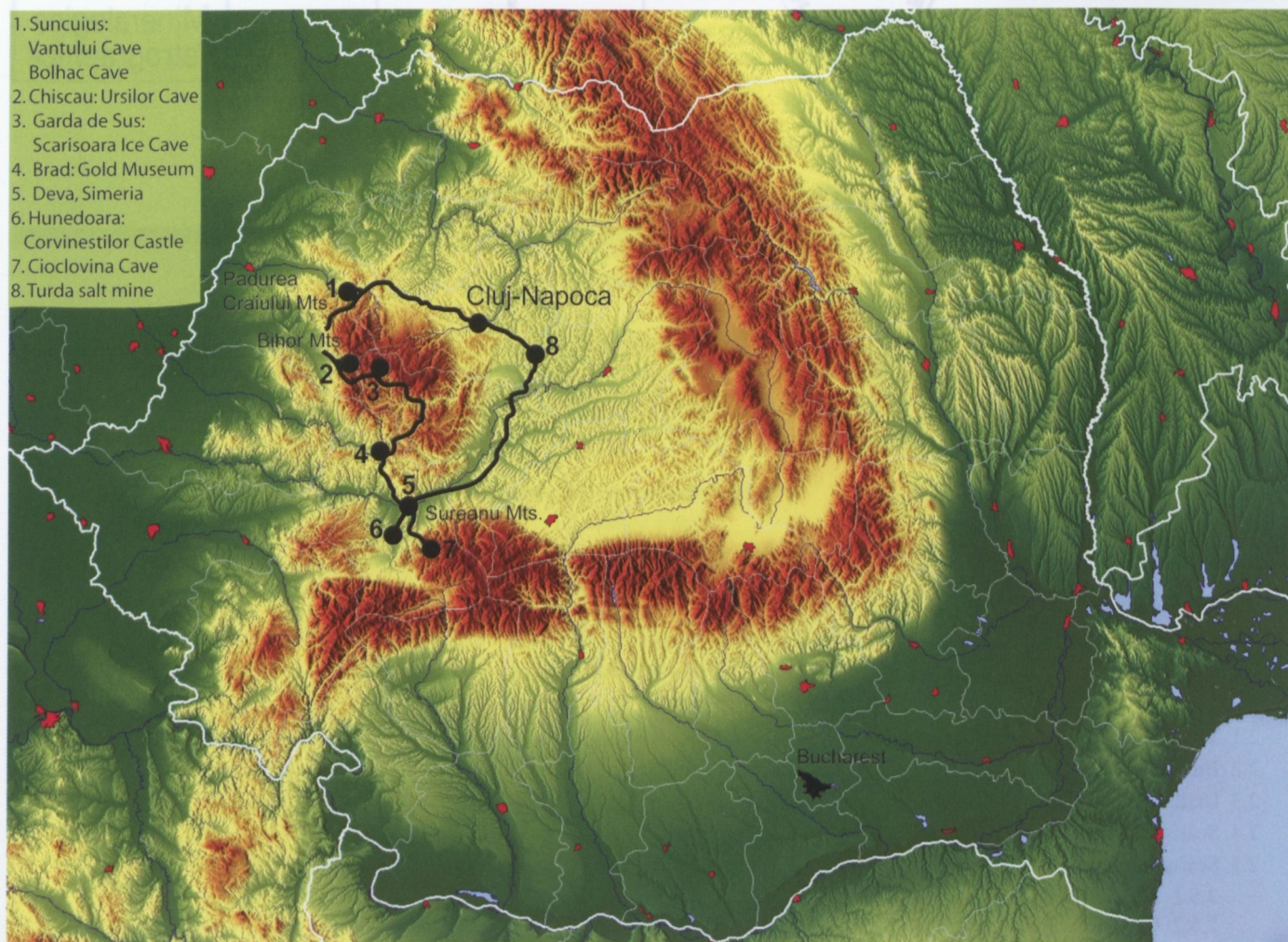


Fig. 1. Route of the IMA2010 RO4 field trip (Cave minerals, Romania). Location of Pădurea Craiului and Bihor massifs within the Apuseni Mountains.

- A Triassic carbonate sequence includes up to 1500 m of Anisian limestones, dolomites, and Ladinian limestones, underlain by Permo-Werfenian non-karst rocks.
- A Jurassic carbonate sequence, averaging 150–200 m in thickness, consists of Middle and Upper Jurassic limestones, separated from the Triassic carbonates by a Lower Jurassic detrital formation.
- A Cretaceous carbonate sequence overlies the Jurassic carbonates discordantly. This sequence includes two units of Lower Neocomian to Aptian limestones, covered by an Aptian to Albian predominantly detrital complex.

Compared to other karst massifs, the PCM hydrological network is characterised by a long evolution, during which stream piracy repeatedly changed flow direction in the valleys. Furthermore, the block tectonics have turned the whole unit into a mosaic-like setting, with karst/non-karst formations alternating and likewise forcing karst drains along distinct alignments. Presently, all rivers are tributaries to either the Crişul Repede in the north, or to the Crişul Negru to the south and southwest.

The great variety of rocks making up the geological structure and their mosaic-like disposition (a result of advanced tectonic

processes that have affected the massif) are expressed morphologically by a chaotic relief that generally lacks any unique features. A massive, upstanding relief, including sandstones, conglomerates, and eruptive rocks, alternates with a lower relief of karst catchment depressions and the flat landscape characteristic of karst plateau that are dotted with sinkholes (Racoviţă *et al.*, 2002).

1.1 Karst landforms

Although in the PCM the carbonate rocks outcrop only on 425 km², the karst displays a rich variety of landforms ranging from the small-scale micro-solutional features such as karren (*lapies*) to large karstic catchment depressions. The most common exokarst features in the PCM are the *dolines*. Imaşul Bătrânului, Igreţ, Runcuri, and Răcaş are only a few of the plateaus where the density is greater than 60 dolines/km². Dolines are bowl-shaped depressions ranging in diameter from a few to several hundred meters, whereas their depths may range from 1–2 m to more than 100 m. They may occur

isolated or in groups. Genetically, most of the dolines in the PCM originate from dissolution processes. Over restricted areas (Damiş, Ponoraş, and Acre depressions), subsidence and collapse (Igriş Plateau) dolines may also be found (Rusu, 1988). Doline plains are widespread on all karst plateaus.

As in most karst regions, the organised surface network of permanent flow is lacking in the PCM. However, a few rivers (Crişul Repede, Iadului, Brăţcuţa, Topa-Râu, etc.) cross partly or entirely on the karst areas forming *transverse valleys*. These valleys are often steep-sided and may occur as spectacularly narrow gorges, punched by numerous caves.

Paleokarst features in PCM have been documented in a few caves (e.g., Vântului Cave), however, most were discovered during mining activities in the region. An episode of continental evolution in the Upper Triassic generated various karst features (lapies, dolines, uvalas) that were subsequently covered by red clays containing limestone blocks, sandstone, and lenses of fire-clay. A similar continental evolution took place after the deposition of the Upper Jurassic limestone. Karstification of this carbonate unit occurred during the Lower Cretaceous. Residual deposits, later transformed into bauxite, filled up most of the karst landforms (lapies, dolines and shafts).

1.2 Endokarst

In addition to the karst landforms that make Pădurea Craiului Mountains so special, also occurring are a great number of caves and potholes (over 1200). Many of these are well decorated or host important mineralogical, archaeological, and/or paleontological remains. Examining a large number of caves (over 750) one can conclude that these are mainly *drawdown* or *invasion vadose* caves (Ponoraş, Gălăşeni, Cornilor, Toaia, Săncuţa, Stanu Foncii, Pobraz etc.) or *water table* caves (Vântului, Vadu-Crişului, Ciur-Izbuc). Rising of geothermal waters from deep aquifers are probably responsible for the genesis of a limited number of vertical cavities (e.g., Betfia Shaft near I Mai Spa).

2. Field stops

2.1 Vântului (Wind) Cave at Şuncuiuş

Vântului Cave is located in the northern part of Pădurea Craiului Mountains, 2 km upstream the mining locality of Şuncuiuş, in a spectacular section of the Crişul Repede river's gorge. The entrance stands at 320 m asl, respectively at only 19 m relative elevation, in the left bank of the river. Vântului Cave spreads on four karstification levels, the lower one being active (Bleahu *et al.*, 1976; Szilágyi *et al.*, 1979). The main passage network stretches parallel to the Mişid Valley and follows the main features of the syncline west of the valley that is cut in the hinge line of an anticline (Vălenaş & Iurkiewicz, 1980/81). Presently, it is Romania's longest cave with surveyed passages of over 51 km (Szilágyi Palkó *et al.*, 2007; Fig. 2).

Climatological investigations undertaken by Onac & Racoviţă (1992) revealed a unidirectional thermocirculation, the cave entrance acting as the lower opening. Along the first 400 m of the cave, during the winter, a seasonal disturbance microclimate is established. In summer (downflowing conditions) the cold air ($\sim 9^\circ\text{C}$) is blown out the cave, hence the name Vântului (Wind) Cave.

The cave is cut in white, poorly metamorphosed Ladinian (middle Triassic) limestone, unconformably overlain by sandstones, microconglomerates and lenses of fireclay of Lower Jurassic age. These transgressive series contain concentrations of pyrite and marcasite, which play an important role in the genesis of the gypsum deposits throughout the cave. Secondary pyrite and marcasite are also present in the Ladinian limestone.

The cave's main morphologic features are the breakdown piles and the meanders. The latter, well individualised in the 2nd and 3rd levels, reach a spectacular climax within the *Racoviţă Meanders* (Coman & Crăciun, 1978). They have been studied by Şerban (1984) who emphasised an alternation of cross-section morphology of the primary conduit, from

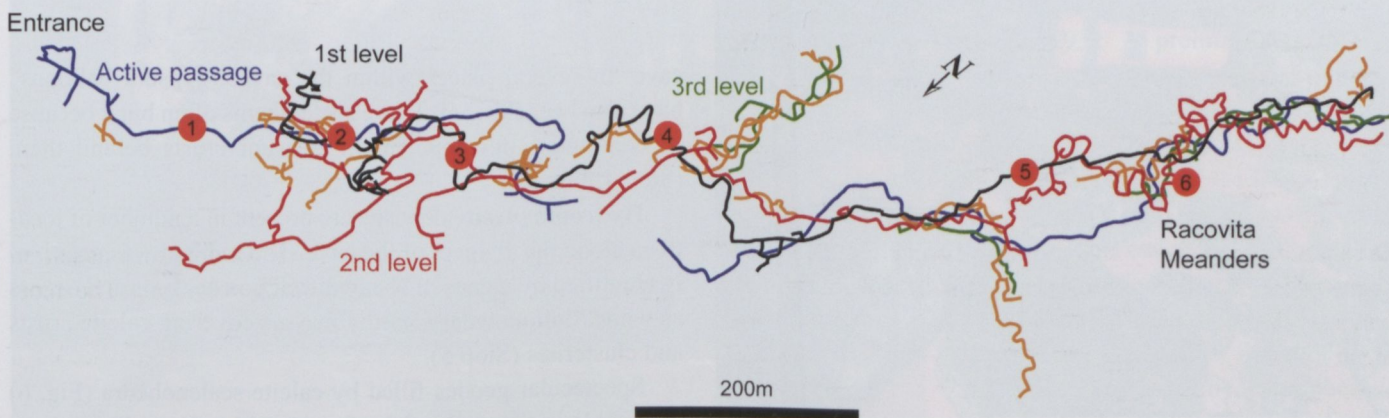


Fig. 2. Simplified map of Vântului Cave, showing the in-cave field trip stops (1 to 6). Various cave levels are colour-coded (adapted from Szilágyi Palkó *et al.*, 2007, by permission).

elliptical to canyon types; this suggests both vertical and horizontal meandering. Such down-cutting is considered by the above-mentioned author as rather typical for karst drains, in which pipe-full flow conditions may generate vertical meandering, analogous to the horizontal ones, which characterises free-surface flow conditions.

Black, earth-like deposits that cover gravel and boulders in the underground stream of the cave (Stop 1, Fig. 3) are mainly composed of **birnessite**, **romanechite**, **todorokite** and other poorly-crystallised manganese oxide and hydroxides as well as **goethite** and kaolinite (Onac, 1996, 1998; Diaconu & Morar, 1997). Scanning electron microscope and EDX analyses performed on the black Fe-Mn precipitations show the material to have concentrated considerable amounts of REEs (La, Ce, Sm, Nd) in iron-rich spheres that build up botryoidal aggregates. The correlation of $^{143}\text{Nd}/^{144}\text{Nd}$ ratio for 6 different samples indicates that the REEs were concentrated in the cave environment after being leached from bauxitic and red residual clays from above the cave. Based on our observations we conclude that an increase in pH resulted in adsorption of REE onto the surface of Fe-Mn minerals (Onac *et al.*, 1997). Furthermore, four species of bacteria and one fungus species have been identified in the black sediments of the Vântului Cave using molecular methods. Three of the bacterial species (*Hyphomicrobium* sp., *Pedomicrobium fusiforme*, *Pedomicrobium manganicum*) and *Cladosporium* sp. are known to mediate the oxidation and precipitation of manganese by enzymatic or nonenzymatic mechanisms in different environments. *Sphingomonas mali* could possibly be another bacterium that helps in the manganese precipitation in the Vântului Cave (Manolache & Onac, 2000). This biologically mediated process is likely to be controlled by the pH



Fig. 3. Boulder covered by black Mn-Fe-rich deposits in Vântului Cave (photo: A. Palmer).

and/or Eh conditions existing within the subterranean stream environment. A possible implication of these microorganisms in the retention of above-mentioned REEs within the black sediments is also possible.

Beside its length, the cave is known for the variety of minerals building up its speleothems. Among carbonates, Viehmann (1975) and Onac (1992, 1996) have mentioned calcite and aragonite. The former is present in a wide range of speleothems: stalactites, stalagmites, columns, crusts, flowstones and helictites. **Aragonite** forms helictites and branch-like aggregates made up of very fine needle crystals (Stop 2).

Gypsum, the only representative of the sulfate group, forms crusts, anthodites, flowers (Stop 3, Fig. 4), as well as needle-like prismatic crystals (Onac, 1991). Gypsum is considered to be genetically related to SO_4^{2-} rich solutions generated by seepage waters that leached sulphide-rich sections in the overlying detrital formations. This was confirmed by $\delta^{34}\text{S}$ values (between -1.1 and $+1.0\%$ CDT) obtained on six samples from various locations along the upper galleries of the



Fig. 4. Gypsum flower (photo: B. Onac).

cave. In several places within the cave, “gypsum balloons” have also been noticed. These speleothems often burst because of continuous development of gypsum crusts behind them (Stop 4, Fig. 5).

Hydromagnesite deposits are present in a number of locations along the 1st level of the cave. The mineral was positively identified by means of X-ray diffraction analysis and occurs as white, dull, powdery, earthy masses covering calcite crusts and clusterites (Stop 5).

Spectacular geodes filled by calcite scalenohedra (Fig. 6) are visible in the walls of the *Racovița Meanders*. These crystals seem to fill paleokarst voids, which were later dissected by the newly formed cave galleries (Stop 6).



Fig. 5. Gypsum balloons (photo: B. Onac).

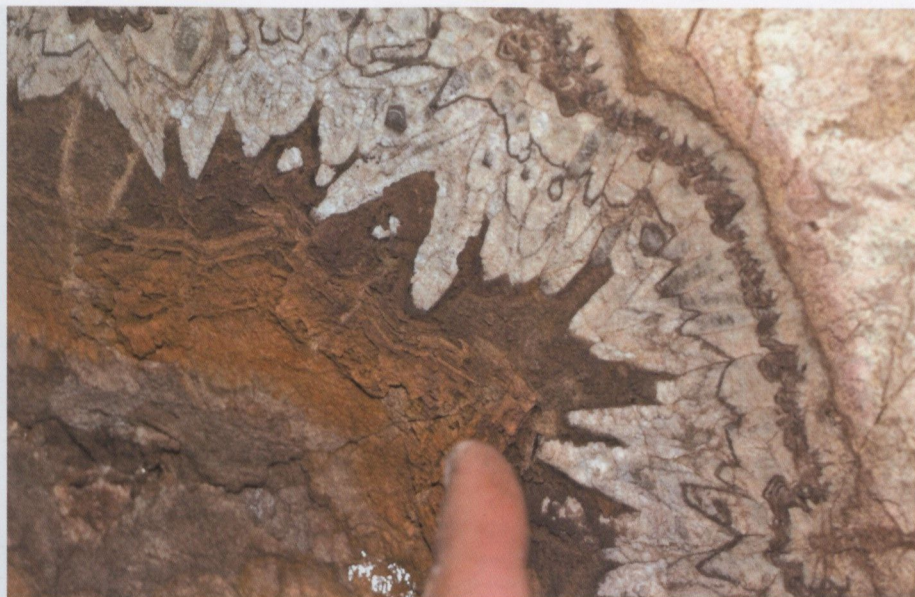


Fig. 6. Geode filled with calcite crystals (Racovița Meanders) (photo: B. Onac).

2.2 Bolhac Cave at Șuncuiuș

Bolhac Cave is located some 2.5 km upstream from the village of Șuncuiuș. The entrance, situated only 1 m above

the level of Crișul Repede River, represents an impressive arch (33×20 m in size), which opens on the left bank of the river (Fig. 7). The cave's total length is ~1.5 km (Fig. 8). Its galleries are cut in

white Ladinian reef limestone, which is transgressively overlain by Liassic sandstone and quartz microconglomerates within which lenses of kaolinitic clays and pyrite are to be found. Due to this geological setting, the bed of the cave stream is covered over a length of ~195 m (Stops 1–3, Fig. 8) by white-yellowish, jelly-like deposits (Fig. 9). The thickness of the deposit increases with depth. During periods of draught, the deposit is more yellowish orange in colour (probably more iron oxides/hydroxides are precipitated), whereas in the rest of the time it is mostly white.

Complex chemical and mineralogical investigations showed the material is an amorphous, unknown hydrated K-Al sulpho-silicate material (Ghergari & Onac, 1993). A preliminary chemical analysis shows the following composition (wt%): Al_2O_3 : 48.17, SiO_2 : 8.51, SO_3 : 13.55, K_2O : 1.5, Fe_2O_3 : 1.26, CaO : 0.49, TiO_2 : 0.26, MnO : 0.12, MgO : 0.15, Na_2O : 0.2, P_2O_5 : 0.18. The DTA curve shows a double endothermic effect at 100 and 200 °C (water release), two other closely linked endotherms at 830 and 880 °C (release of OH^- , SO_3 , and CO_2) respectively, followed by an exothermic peak at 940 °C, which marks the formation of mullite $[\text{Al}_{(4+2x)}\text{Si}_{(2-2x)}\text{O}_{(10-x)}]$ where $x = 0.17$ to 0.59 . The material is



Fig. 7. Entrance in the Bolhac Cave (photo: B. Onac).

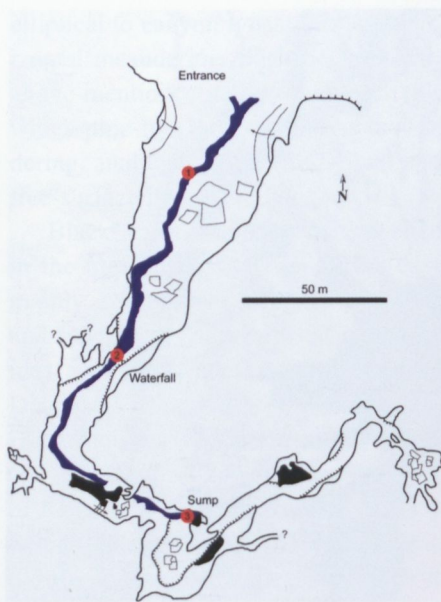


Fig. 8. Partial map of the Bolhac Cave showing the in-cave field trip stops (1 to 3).



Fig. 9. Unknown material precipitated in the Bolhac Cave streambed (photo: B. Onac).

still under investigations and will soon be submitted to the IMA Commission on New Minerals, Nomenclature and Classification.

Strongly acidic cave waters (pH 3 to 4), rich in aluminium, silica gels, potassium, and sulphates (leached from fire-clay lenses) are progressively neutralised (limestone acts as buffer), along the underground stream favouring the precipitation of this peculiar gelatinous material. The cave is also famous for its archaeological artefacts found near the entrance during the emplacement of the suspended bridge.

If time will allow, another cave with similar depositions will be visited in the nearby vicinity.

2.3 Urşilor (Bears') Cave at Chişcău

The Urşilor Cave is located in the north-western part of Romania (80 km south-east of Oradea) at 482 m asl, on the west-facing slope of Apuseni Mountains. The cave has no known natural entrance, being accidentally discovered by Traian Curta in 1975 after blasting in a marble quarry. The first exploration revealed that the cave preserved important pale-

ontological remains (mainly *Ursus spelaeus*) and also a great variety of speleothems. Consequently, it was gated and fitted for tourism, and has become the most important show cave in Romania.

The cave is carved in Upper Jurassic (Tithonic) thermally recrystallised limestone and consists of 1500 m of large passages developed along two distinct levels (Fig. 10a). The lower one, still active, hosts most of the cave bear remains; therefore it is preserved as a scientific reserve and the access is strictly prohibited. The upper level is no longer hydrologically active; it is highly decorated and therefore it is part of the show cave (Fig. 10b; Rusu, 1981). The two artificial entrances are well sealed in order to preserve the original cave microclimate so that the upper level remains free from vigorous airflow and maintains a stable temperature. The mean annual temperature in the cave is 9.8 °C (ranging between 9.5 and 10.1 °C), and the relative humidity is around 100% (Racoviţă *et al.*, 2003).

The speleogenetic evolution of Urşilor Cave (Figs. 11 a–d) is closely linked to the lowering of the local base level. Analysing its longitudinal section and following the disposition of

the passages, as well as morpho-hydrographic elements both underground and at the surface, one can reconstruct the paleogeographic evolution of the region. By such an approach, Rusu (1981) identified the following speleogenetic stages:

1. The water infiltrating from the karst plateau above the future cave fed an unconfined aquifer that discharged at the surface through the *Twisted Passage* (Fig. 11a, I-1). The passage is located 50 m above the present base level, so it appears that in the first stage of cave evolution, the base level established by the local Miocene Bay was much higher. Therefore, by that time the Lower Passage (*Scientific Reserve*), "*Emil Racoviţă*" and *Candles* passages began their formation at or below the water table.
2. As the water table dropped, the water abandoned the *Twisted Passage* (Fig. 11a, II). The surface stream now entered the cave using a different sinking point (Fig. 11a, 2).
3. In the next stage, after a new lowering of the Pliocene Pannonian Lake, the water level also dropped in what is now the Beiuş Depression (Fig. 11b, III), and the cave stream was

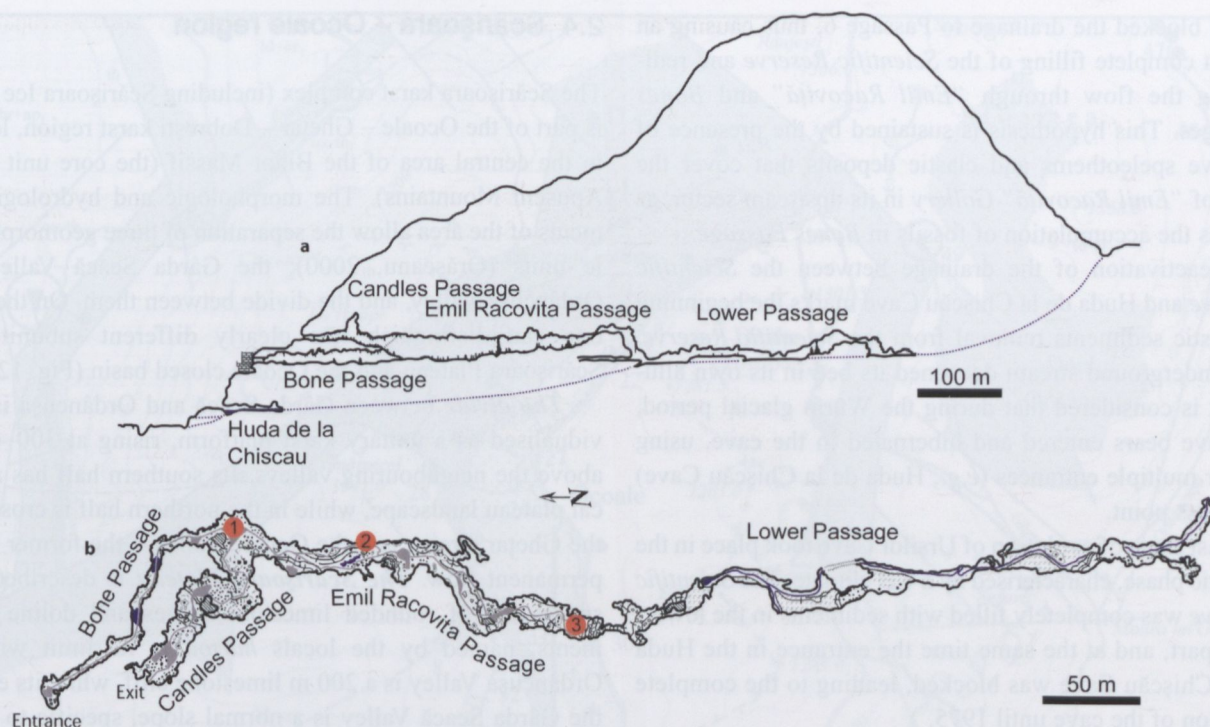


Fig. 10. Map of Urșilor Cave. a) profile view; b) plan view showing the in-cave stops (1 to 3).

drained to the surface through the *Bones Passage* (Fig. 11b, 3). At the beginning, this passage was mainly below the water table, but later it became air-filled (vadose conditions). Based on the morphology of the ceiling (numerous cupolas and blind screw-like passages) one can argue that a hypogenic stage was also present during this stage of cave evolution. By draining the cave stream via *Bones Passage*, the *Candles Gallery* was completely abandoned by water. The only passage still active at that time was "*Emil Racovița*" Gallery.

4. During the late Neogene the extension of the Pannonian Sea decreased significantly, causing the complete drain of its gulfs (including Beiuș Depression). After this event, the cave stream abandoned the *Bones Passage* and emptied at the level of Crăiaș Valley, which represents the base level ever since (Fig. 11c, 6). Karst conduit flow in *Scientific Reserve* and Passage 6 in Figs. 11c–d was still under phreatic conditions.
5. Following the uplift of the Bihor Mountains the flow regime in the cave changed to a vadose one. The altitude of the discharge point changed and in order to keep pace with the rapid downward progress of Crăiaș Valley, the cave stream now begins the incision of floor in the *Scientific Reserve* and Passage 6, transforming the gallery into canyons (Fig. 11d, 5 & 6).
6. During the Pleistocene, speleothem deposition in the upper passages was extremely active, while in the *Scientific Reserve* several infilling and reactivating phases occurred as a consequence of the outside climatic variations. During the last interglacial, the amount of sediments was so large

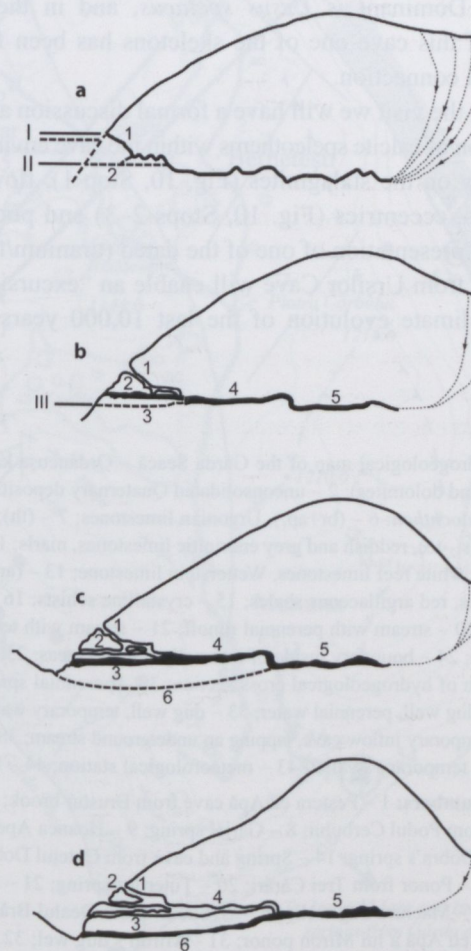


Fig. 11. Evolution of Urșilor Cave. 1 – Twisted Passage; 2 – Candles Passage; 3 – Bones Passage; 4 – "*Emil Racovița*" Gallery; 5 – *Scientific Reserve*; 6 – Huda de la Chișcău Cave and an unexplored passage (after Rusu, 1981, modified).

that it blocked the drainage to Passage 6, thus causing an almost complete filling of the *Scientific Reserve* and redirecting the flow through “*Emil Racoviță*” and *Bones* passages. This hypothesis is sustained by the presence of massive speleothems and clastic deposits that cover the floor of “*Emil Racoviță*” *Gallery* in its upstream sector, as well as the accumulation of fossils in *Bones Passage*.

7. The reactivation of the drainage between the *Scientific Reserve* and Huda de la Chișcău Cave marks the beginning of clastic sediments removal from the *Scientific Reserve*. The underground stream deepened its bed in its own alluvia. It is considered that during the Würm glacial period, the cave bears entered and hibernated in the cave, using one or multiple entrances (e.g., Huda de la Chișcău Cave) as access point.
8. The last stage of evolution of Urșilor Cave took place in the Atlantic phase, characterised by a wet climate. The *Scientific Reserve* was completely filled with sediments in the lowermost part, and at the same time the entrance in the Huda de la Chișcău Cave was blocked, leading to the complete isolation of the cave until 1975.

From a paleontological point of view, over 40 species of Pleistocene and Holocene mammals have been identified in the cave. Dominant is *Ursus spelaeus*, and in the Lower Passage of this cave one of the skeletons has been found in anatomical connection.

During the visit we will have a formal discussion about the precipitation of calcite speleothems within the cave environment, particularly on the stalagmites (Fig. 10, Stop 1), flowstones, anemolites, eccentrics (Fig. 10, Stops 2–3) and pool spars. A detailed presentation of one of the dated (uranium/thorium) stalagmite from Urșilor Cave will enable an “excursion” into the paleoclimate evolution of the last 10,000 years in NW Romania.

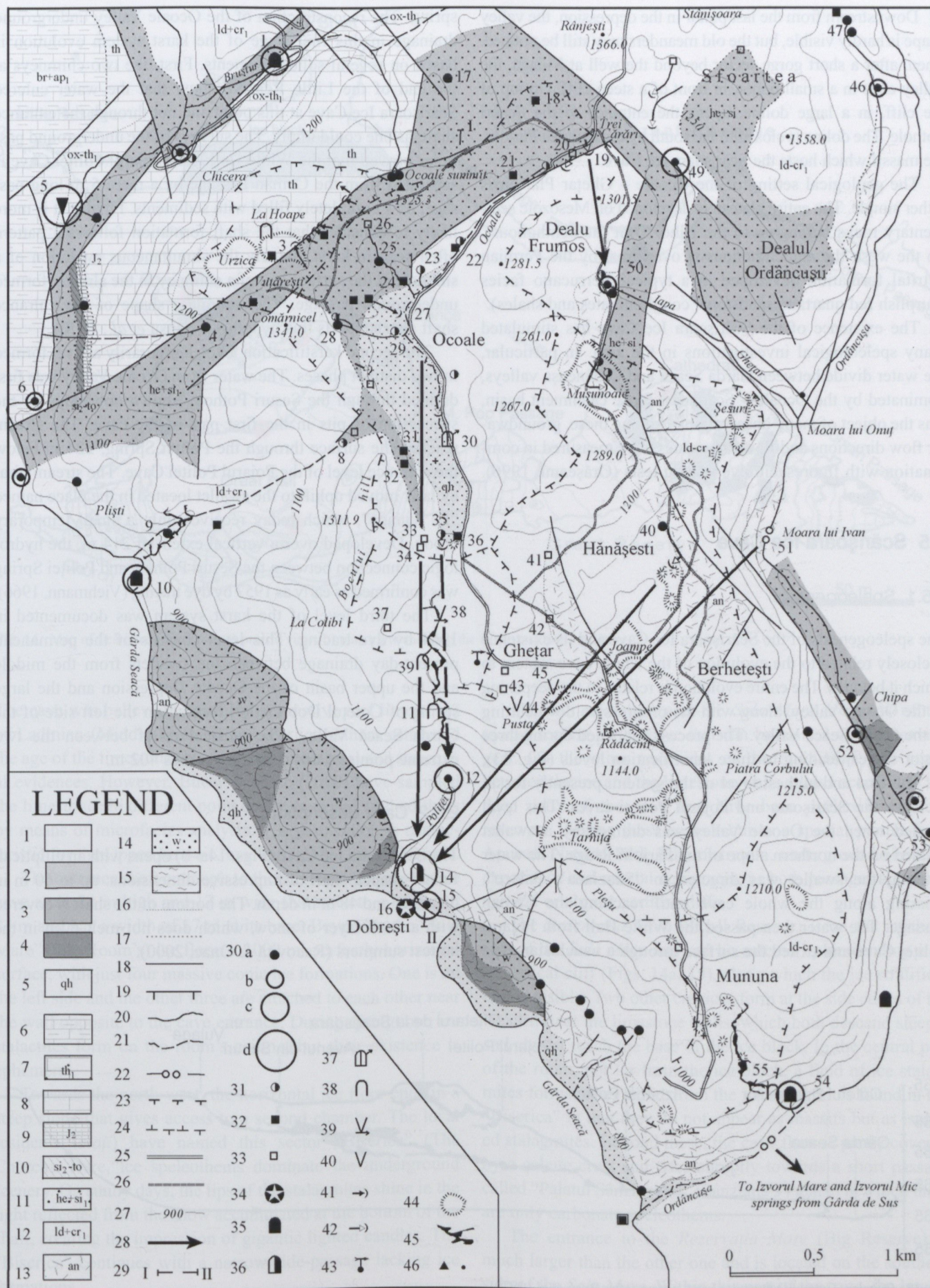
2.4 Scărișoara – Ocoale region

The Scărișoara karst complex (including Scărișoara Ice Cave) is part of the Ocoale – Ghețar – Dobrești karst region, located in the central area of the Bihor Massif (the core unit of the Apuseni Mountains). The morphologic and hydrologic elements of the area allow the separation of three geomorphologic units (Orășeanu, 2000): the Gârda Seacă Valley, the Ordâncușa Valley, and the divide between them. On the latter one can distinguish two clearly different subunits: the Scărișoara Plateau and the Ocoale closed basin (Fig. 12).

The divide between Gârda Seacă and Ordâncușa is individualised as a unitary karst platform, rising at 300–400 m above the neighbouring valleys. Its southern half has a typical plateau landscape, while in the northern half is crossed by the Ghețar stream and the Ocoale Valley – the former with a permanent flow. **The Scărișoara Plateau** is described by a succession of rounded limestone ridges and doline alignments, named by the locals *hârtoape*. Its limit with the Ordâncușa Valley is a 200 m limestone cliff, while its edge to the Gârda Seacă Valley is a normal slope, specific to alpine areas. **The Ocoale closed basin** was modelled by the stream with the same name between the Ocoale – Ordâncușa hill ridge to the north and the Culmea Pârjolii summit to the south. The Ocoale stream forms below the Ocoale Hill (1324 m asl) from several springs, which generate a large marshy area developed on impervious rocks. After flowing a short distance at surface, the water disappears underground through several ponors and diffuse losses scattered along some kilometres. In this final sector, the stream meanders in a large depression whose flat bottom is mostly flooded both during heavy rains and at snow melting. The waters reappear at the surface at two different locations: Poliței Spring and Cotețul Dobreștilor resurgence.

Fig. 12. Hydrogeological map of the Gârda Seacă – Ordâncușa karst region (from Orășeanu, 1996 by permission). **Legend:** 1 – Mesozoic carbonate series (limestones and dolomites); 2 – unconsolidated Quaternary deposits; 3 – Mesozoic molasse deposits; 4 – areas devoid of water resources; 5 – (qh), recent alluvia. *Bihor Autochthon*: 6 – (br+ap), Urgonian limestones; 7 – (th), black bedded oolitic limestones; 8 – (ox-th₁), reef limestones; 9 – (J₂), red oolitic limestones; 10 – (si₂-to), reddish and grey encrinitic limestones, marls; 11 – (he+si₁), quartzitic sandstones and conglomerates, argillaceous shales, black limestones; 12 – (ld+cr₁), white reef limestones, Wetterstein limestone; 13 – (an), grey dolomites. *Bihor Autochthon and Gârda Nappe*: 14 – (w), quartzitic sandstones and conglomerates, red argillaceous shales; 15 – crystalline schists; 16 – normal geological boundary; 17 – discordant geological boundary; 18 – fault; 19 – overthrust front; 20 – stream with perennial runoff; 21 – stream with temporary runoff; 22 – karstic loss in river valley labelled with tracer; 23 – limit of internally drained areas; 24 – boundary inside of internally drained areas; 25 – village road; 26 – forest road; 27 – contour line; 28 – proved groundwater flow direction; 29 – direction of hydrogeological cross section; 30 – perennial spring, discharge in l/s: a – under 1; b – 1 to 10; c – 11 to 50; d – 200 to 350; 31 – temporary spring; 32 – dug well, perennial water; 33 – dug well, temporary water; 34 – degassing hypothermal spring; 35 – perennial outflow cave; 36 – temporary outflow cave; 37 – temporary inflow cave, tapping an underground stream; 38 – fossil cave; 39 – pothole tapping an underground stream; 40 – fossil pothole; 41 – perennial swallet; 42 – temporary swallet; 43 – meteorological station; 44 – karst depression, doline; 45 – cave passage; 46 – hill.

Key of the numbers: 1 – Peștera cu Apă cave from Brustur brook; 2 – Spring of Băii brook; 3 – Big ponor from La Hoape; 4 – Știubei spring; 5 – Tăuz spring; 6 – Spring from Podul Cerbului; 8 – Gârjel spring; 9 – Hoanca Apei spring and cave; 10 – Peștera cu Apă from La Tău; 11 – Pojarul Poliței Cave; 12 – Poliței spring; 13 – Dobra’s spring; 14 – Spring and cave from Cotețul Dobreștilor; 15 – Mill’s spring; 16 – Feredeș spring; 17 – Negreștilor dug well; 18 – Jimboiești dug well; 19 – Ponor from Trei Căări; 20 – Țuțerilor spring; 21 – Debii spring; 22 – Oncheștilor dug well and spring; 23 – Costenilor spring; 24 – Buleștilor dug well; 25 – Maciura dug well; 26 – “Izbucul” from Dealul Brăzdeștilor spring; 27 – Ponor of Gogului brook; 28 – “La Izvoare” spring; 29 – Mii spring; 30 – Groapa cu Apă a lui Miron ponor; 31 – Miron’s dug well; 32 – Ilii Florea’s dug well; 33 – “Apa Rece” dug well; 34 – Fântâna de După Deal dug well; 35 – Spring and ponor at Vuiaga Veche; 36 – Dug well at Vuiagă; 37 – Dug well at Șesuri; 38 – Pothole at Șesuri; 39 – Ghețarul de la Scărișoara ice cave; 40 – Troaca spring; 41 – Bărâcia dug well; 42 – “Apa din Cale” dug well; 43 – Dug well from Gard de la Dubi; 44 – Pothole from Pociociște; 45 – Pusta pothole; 46 – Old dug well and spring from Dăgârtești; 47 – Bolf spring; 49 – Ghețarului spring; 50 – Iapa spring; 51 – Losses in flow of Ordâncușa brook from Ivan’s Mill; 52 – Spring from Chipa’s Mill; 53 – Țeghe spring; 54 – Poarta lui Ioanele Cave; 55 – Zguraști Cave.



Downstream from the last ponor in the depression, the valley shape is hardly visible, but the old meanders may still be noticed. Then, after a short gorge sector beyond the well at Vuiagă, the valley ends in a small ponor, in front of a steep cliff. On top of the cliff, in a large doline, opens the entrance to the Șesuri Pothole. The doline is closed to the south by the Culmea Pârjolii, the massif which hosts the Scărișoara Ice Cave.

The geological setting of the Ocoale – Ghețar Plateau is rather simple. The entire plateau is developed on Mesozoic sedimentary rocks belonging to the Bihor Unit (autochthonous). To the west, the autochthonous is overthrust by the Permian detrital formation developed in a typical Verrucano facies (purplish red quartzite sandstone, conglomerates and shales).

The existence of the Scărișoara Ice Cave has stimulated many speleological investigations in the area. In particular, the water divide between Gârda Seacă and Ordâncușa valleys, dominated by the Ocoale – Scărișoara close catchment basin, was the object of many observations. Among these, groundwater flow directions and flow rate values were measured in combination with fluorescein dye tracing tests (Orășeanu, 1996).

2.5 Scărișoara Ice Cave

2.5.1 Speleogenesis

The speleogenesis of the Scărișoara Ice Cave and its existence is closely related to the evolution of the whole cave system to which it belongs. The entire evolution is related to the deepening of the Ocoale Valley, along with the progressive downcutting of the Gârda Seacă Valley. The process happened during three major stages, leading to three karstification levels (Fig. 13).

The first and highest level of the system, presently fossil, includes the Scărișoara and Pojarul Poliței caves. This level formed when the Ocoale Valley was drained by a swallet located on the northern slope of the Pârjolii Ridge. The water entering the swallet was directed to “Sânziana’s Palace”, crossing along the whole cave until reaching the Coman Passage. The water then passed the White Hall from Pojarul Poliței Cave and exited the surface through a vaclusian-type

spring. The reconstruction of the Ocoale Valley underground drainage in this first stage of the karst system evolution is based on several solid arguments. First, the two chimneys at the end of the Little Reserve show that the water entered Scărișoara Ice Cave at this point and not through the entrance shaft, as one could imply. The surveys of the underground passages proved that the White Hall from Pojarul Poliței Cave is separated from the Coman Passage by a mere 5 m long passage, now completely filled with sediments. Finally, it is more likely to consider that the shaft formation follows a pattern often seen in karst, namely the simultaneous evolution of a sinkhole at the surface and of a chimney in the already formed underground passage. The hourglass shape of the entrance shaft also supports this hypothesis (Rusu *et al.*, 1970).

The second karstification level, temporarily active, formed in two distinct phases. The water from Ocoale Valley was first drained through the Șesuri Pothole, shown nowadays by the succession of pits in the first part of the cave. The stream reached the surface through the Poliței Spring, 224 m below the entrance level of the Pojarul Poliței Cave. The stream piracy later moved uphill to the swallet located in the place named “La Vuiagă”, which today receives only a small temporary brook. Developed over a vertical extent of 214 m, the hydrologic connection between the Șesuri Pothole and Poliței Spring was confirmed as early as 1957 by dye tracing (Viehmänn, 1966).

The third level of the karst system was documented in 1964 by dye tracing. This level consists of the permanent present-day drainage between the swallets from the middle and the upper basin of the Ocoale Depression and the large spring of Cotețul Dobreștilor, located on the left side of the Gârda Seacă Valley. The vertical relief between the two extreme points of this drainage reaches 402 m.

2.5.2 Cave description

The Scărișoara Ice Cave (Figs. 14a–b) opens with an elliptical, funnel-shaped shaft of impressive dimensions: up to 60 m in diameter and 48 m in depth. The bottom of the shaft is covered with a thick layer of snow, which does not melt even in the hottest summers (Racoviță & Onac, 2000).

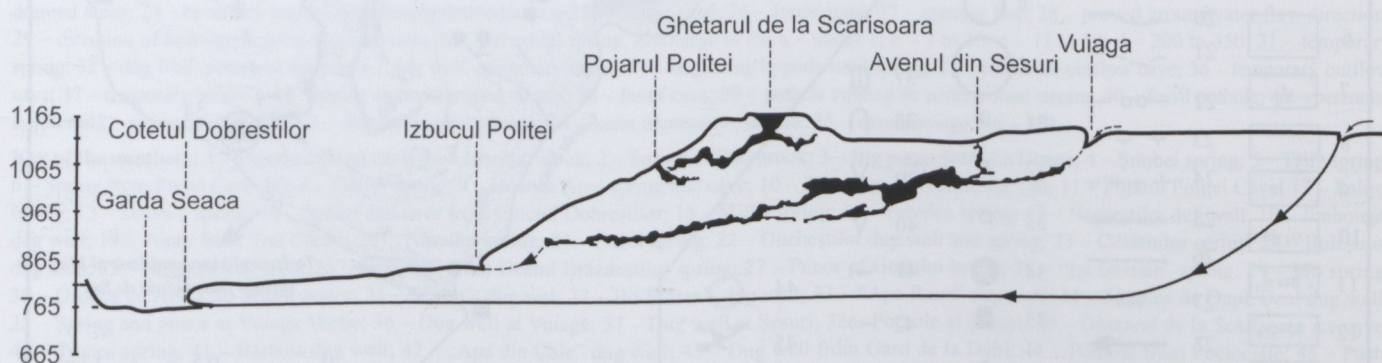


Fig. 13. Ocoale – Cotețul Dobreștilor karst system (after Rusu *et al.*, 1970).

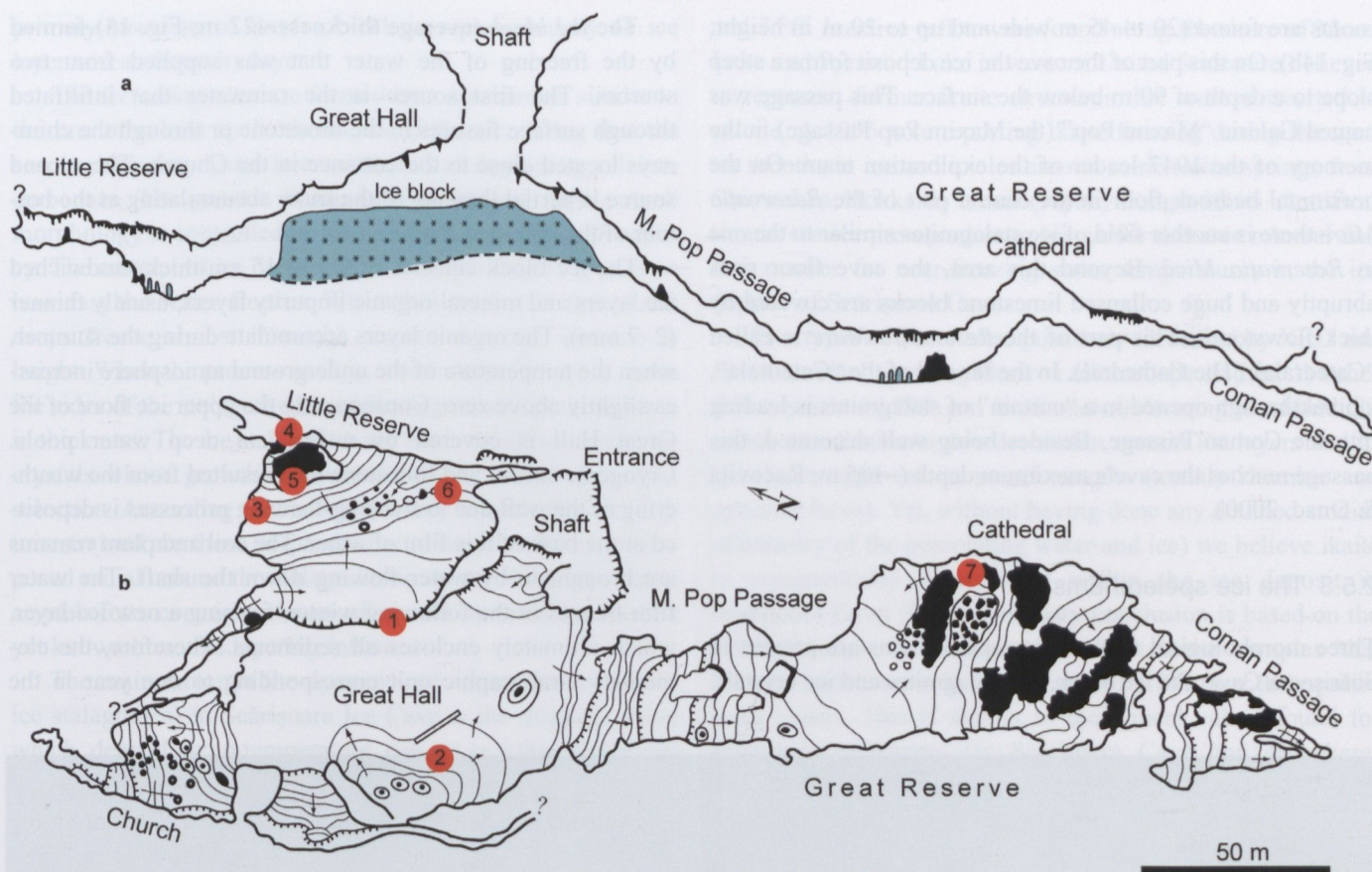


Fig. 14. Map of Scărișoara Ice Cave. a) profile view; b) plan view showing the in-cave stops (1 to 7).

The cave was believed to develop in massive reef limestones of Ladinian (Middle Triassic) age. Earlier authors estimated the age of the limestone by using paleontological and structural evidences. However, Bucur & Onac (2000) have sampled the limestones in different point of the cave and studied them by means of microfacies analysis. The association is characteristic for the Upper Jurassic, most probably Lower Tithonic.

The entrance shaft connects to the west with an impressive cave arch, 24 m high and 17 m wide that rises to a height of 24 m and has a width of 17 m at its base. Beyond is the “Sala Mare” (Big Room’s) ice floor, a 3000 m² perfectly horizontal surface, with just four massive conic ice formations. One is on the left side and the other three are attached to each other near the wall opposite to the cave entrance. During springtime, ice stalactites form on the room’s ceiling, but their existence is ephemeral.

Towards the north-west, the horizontal ice floor ends in a steep slope that gives access to a second chamber. The local residents (*moți*) have named this sector “Biserica” (The Church). Here, ice speleothems dominate the underground scenery. On sunny days, the tips of the stalagmites shine in the light reflected from the snow accumulated at the bottom of the shaft, creating the impression of gigantic lighted candles. The “Biserica” continues with a narrow side-passage lacking ice formations.

The entrance shaft and the *Sala Mare* are parts of the tourist section of the cave that can be visited without caving gear. On the other two sides of the *Sala Mare*, the space between the ice and the limestone walls allows access into the deep parts of the cave that have been declared scientific reserves. Visiting these areas requires a special permit from Apuseni Natural Park Administration, underground climbing experience and special equipment, as both passages are either vertical or almost vertical cliffs.

The *Rezervația Mică* (Small Reserve) is on the northern side of the *Sala Mare* and can be entered by descending a 15 m vertical cliff (Figs. 14a, 15), along which the ice stratification is visible. Two other crevices form at the side edges of the ice cliff near the limestone walls, which both descend steeply and almost reach the base of the ice block. In the central part of the room, not far from the ice block, a field of ice stalagmites forms. They differ from the ice stalagmites found in the “Biserica” in that they do not appear as massifs but as isolated stalagmites. Beyond these, the cave floor is partly covered by a calcite crust and rises abruptly towards a short passage called “Palatul Sânzienelor” (Sânziana’s Palace) in which there are only carbonate speleothems.

The entrance to the *Rezervația Mare* (Big Reserve) is much larger than the other one and is located on the southern side of the *Sala Mare*. Within this part of the cave, the largest

rooms are found (20 to 45 m wide and up to 20 m in height; Fig. 14b). On this part of the cave the ice deposit forms a steep slope to a depth of 90 m below the surface. This passage was named Galeria “Maxim Pop” (the Maxim Pop Passage) in the memory of the 1947 leader of the exploration team. On the horizontal bedrock floor in the central part of the *Rezervația Mare* there is another field of ice stalagmites similar to the one in *Rezervația Mică*. Beyond this area, the cave floor rises abruptly and huge collapsed limestone blocks are covered by thick flowstones. This part of the *Rezervația Mare* is called “Catedrala” (The Cathedral). In the far end of the “Catedrala”, a breakthrough opened in a “curtain” of stalagmites is leading into the Coman Passage. Besides being well decorated, this passage reaches the cave’s maximum depth (–105 m; Racoviță & Onac, 2000).

2.5.3 The ice speleothems

Three morphological types of ice speleothems are present in Scărișoara Cave: the ice block, ice stalagmites and ice crystals.

The *ice block* (average thickness ~22 m; Fig. 15) formed by the freezing of the water that was supplied from two sources. The first source is the rainwater that infiltrated through surface fissures in the limestone or through the chimneys located close to the entrance in the Church. The second source is partial thawing of the snow accumulating at the bottom of the entrance shaft.

The ice block consists of 0.5 to 15 cm-thick sandwiched ice layers and mineral/organic impurity layers, usually thinner (2–7 mm). The organic layers accumulate during the summer, when the temperature of the underground atmosphere increases slightly above zero. Consequently the upper ice floor of the Great Hall is covered by a few cm deep water pools. Cryogenic calcite and limestone dust resulted from the weathering of the wall due to freezing-thawing processes is deposited at the base of this film of water. The soil and plant remains are brought in by water flowing down the shaft. The water film freezes in the following winter, forming a new ice layer, which ultimately encloses all sediments. Therefore, the elementary stratigraphic unit corresponding to one year in the



Fig. 15. View of the ice cliff of the *Rezervația Mică* (photo: C. Ciubotărescu).

primary structure of the ice block is represented by an ice layer and an impurity layer.

The *ice stalagmites* are formed by a mechanism similar to the one of calcite speleothems, the difference being that the seeping/dripping water freezes instead of depositing calcium carbonate. The growth of ice stalagmites and their overall morphology is controlled by air temperature and drip frequency. The amount of ice deposited on stalagmite tips depends on how fast the water freezes. When this process is fast, water drops freeze almost instantly, causing a quick increase in height. When the process is slow, water drops first ooze down the sides of the stalagmites, contributing mainly to an increase in thickness. The ice stalagmites are made up of hexagonal ice crystals whose growth is governed by the law of geometric selection. According to this law, the only crystals that develop unrestrained are those perpendicular to the growth axis or disposed radial around the stalagmite tip. In the stalagmite mass, crystals form concentric layers of several cm thick, but it is not yet known how this layering initiates.

The main factor in the dynamics of ice speleothems (*i.e.*, ice stalagmites) in Scărișoara Ice Cave is the dripping water which, depending on temperature, can act as a favourable element for both the growing and melting of ice (Perșoiu, 2004). Between January and April, these speleothems experience a growing phase, whereas between April and December they go through a partial or total melting phase.

Spectacular *ice crystals* (Fig. 14, Stop 1) having hexagonal plate-like morphology have been noticed in early spring and late autumn on the cave walls near the entrance in *Rezervația Mică* and *Mare*. The size of these ice crystals range from 1–2 cm to over 12 cm across. They form when moist, warm air enters the cave and moisture desublimates on the cold walls.

2.5.4 Mineralogy of non-ice speleothems

Scărișoara Ice Cave stands out among the other world's greatest ice caves because of its huge ice block (over 100,000 cubic metres), age (over 4000 years old), and because it hosts not only spectacular ice speleothems, but also a selection of carbonate and phosphate speleothems. Concentrated mostly in the Cathedral, Sânziana's Palace and in the Coman Passage, these speleothems are represented by stalactites, stalagmites, columns, cave pearls, domes, draperies, clusterites, flowstones and gours. The carbonate minerals *calcite*, *aragonite*, *monohydrocalcite* and *hydromagnesite* are deposited as various speleothems from dripping, seeping, splashing and pooling water. Calcite, however, composes the majority of the speleothems. The other three carbonate minerals occur only in one or a maximum of two types of speleothems. To these, one can add the cryogenic calcite (Žák *et al.*, 2008) and the bizarre ikaite (Onac, 2008).

Ikaite is a rare metastable carbonate mineral first identified in submarine reef-like columns growing from the bottom of Ika Fjord (SW Greenland) at temperatures between –1.9

and 7 °C. Inactive tuff towers found along the shore of Mono Lake and Pyramid Lake in western United States are believed to represent former ikaite structures that were converted to calcite. A 1996 note reporting ikaite forming during the winter months in ice and icicles around some saline springs from Shiwakka, Hokkaido Island (Japan) along with its identification in sea ice prompted us to search for this rare mineral that is a marker for near-freezing water temperatures in the ice deposit of Scărișoara Cave.

Two types of ikaite were positively identified by XRD and environmental scanning electron microscope studies: 1) euhedral crystals (< 200 μm in diameter) forming a white-light cream moist mineral powder within certain ice layers and 2) glendonite-type calcite pseudomorphs (mainly rhombic and pyramid faces). Yet, without having done any detailed studies (chemistry of the percolating water and ice) we believe ikaite is cryogenically precipitated within the ice deposit in Scărișoara Cave. This preliminary conclusion is based on the stable isotope measurements on two ikaite samples that showed enrichments in $\delta^{13}\text{C}$ of up to +8.7‰ over the equilibrium values. This is similar to the typical values found for cryogenic carbonates (in Scărișoara Cave and elsewhere) formed during rapid water freezing that is accompanied by swift kinetic CO_2 degassing. The calcite pseudomorphs after ikaite (glendonite) were found at the limit of the ice field in the Big Reserve and their presence seems to be indicative of near-freezing conditions for water and hence useful as paleothermometers, providing a good calibration is established.

Cryogenic cave carbonates (CCC) represent a specific type of speleothems (Fig. 14, Stop 2). Their precipitation proceeds at the freezing point and is triggered by freezing-induced concentration of solutes. Compared to classical speleothems (stalagmites, flowstones), CCC occur as accumulations of loose (uncemented) aggregates. The grain sizes range from less than 1 mm to over 1 cm in diameter. Karst groundwater chemistry and its freezing rate upon entering the cave are responsible for highly variable grain morphology. Rapid freezing of water results in the formation of CCC powders with grain size typically below 50 μm. Slow freezing of water in caves (usually in systems where the CO_2 escape is partly restricted; *e.g.*, ice covered water pools) results in the formation of large mineral grains (Žák *et al.*, 2008).

The studied Scărișoara pearls show a similar trend to the CCC powders from the same cave, but their isotopic values plot on different fields in the $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ diagram (Fig. 16). Therefore, the pearls could not have formed by simple mechanical aggradation of fine-grained calcite (lublinite) supplied by water freezing as speculated by Viehmann (1960, 1967). A different genetic pathway is required. The most plausible explanation is that the calcite of Scărișoara pearls precipitated during water freezing in an open system (with respect to water), *i.e.*, in a system of partial water freezing from which a fraction of non-frozen solution flows away. This is in agreement with their position in the periglacial zone, in front of the

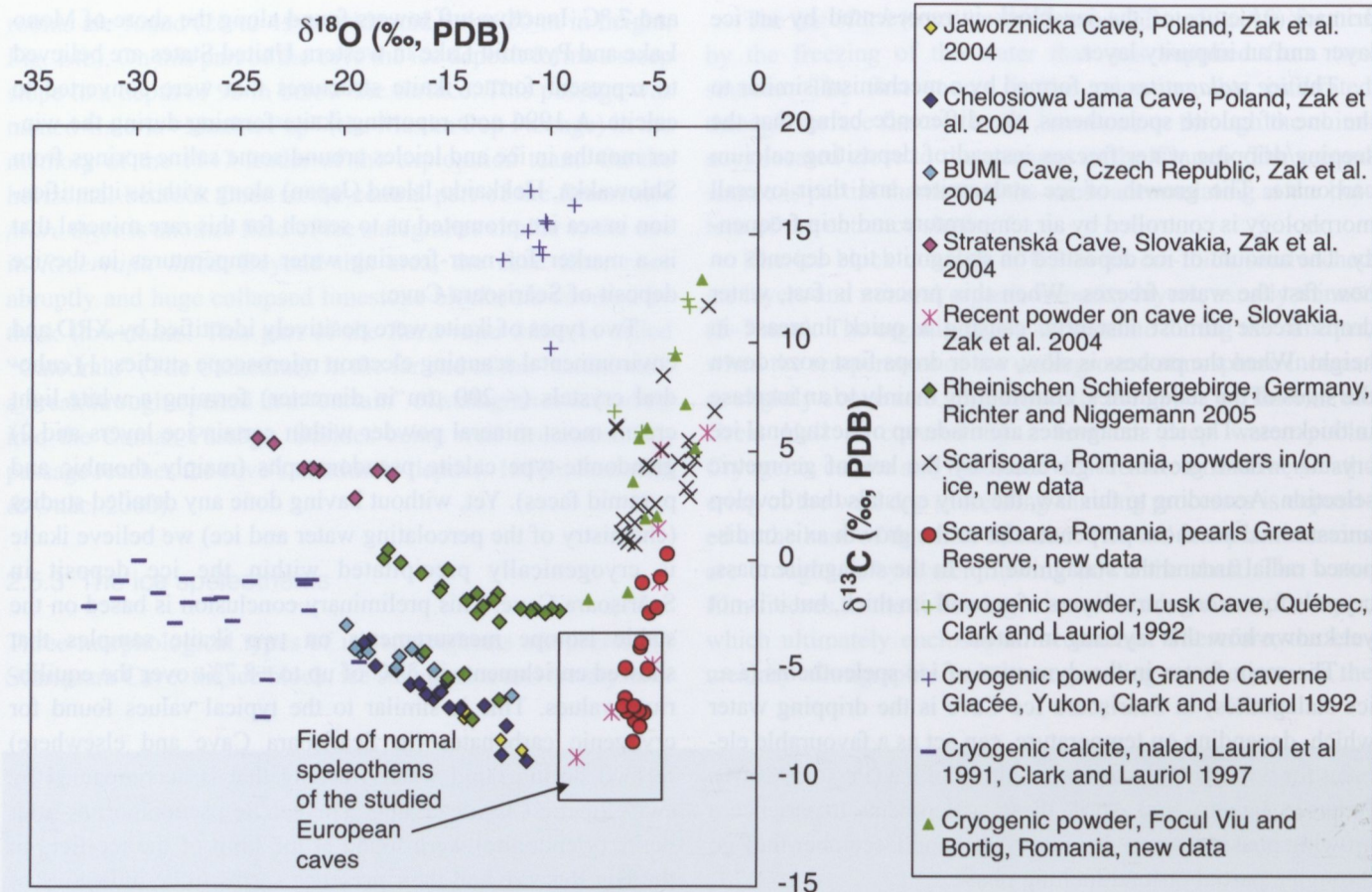


Fig. 16. Isotopic values for cryogenic calcite and pearls in Scărișoara Ice Cave (from Žák *et al.*, 2008).

underground ice mass (Fig. 14, Stop 7; Fig. 17). Also, during summer, these pearls are fed by bicarbonate-rich waters that may precipitate on the surface of the pearls, giving different isotopic values for calcite. Seasonal freezing and melting cycles are the dominant process keeping the individual pearls free, separated from each other, and from the underlying limestone scree.



Fig. 17. Cave pearl nest in the Rezervația Mare, Scărișoara Ice Cave (photo: B. Onac).

The range of carbon and oxygen stable isotope composition of CCC is greater than for a typical carbonate speleothem. Rapid freezing of water accompanied by quick kinetic CO_2 degassing results in large ranges of $\delta^{13}\text{C}$ data of the CCC powders (between -10‰ and $+18\text{‰}$). Slow freezing of water, with restricted CO_2 escape, results in gradual $\delta^{13}\text{C}$ increase (from -9‰ to $+6\text{‰}$ PDB), accompanied by a $\delta^{18}\text{O}$ decrease of the precipitated carbonate (overall range from -10‰ to -24‰). These unusual trends of the carbonate $\delta^{18}\text{O}$ evolution reflect the incorporation of the heavier ^{18}O isotope into the formed ice. The new isotope data on CCC from Scărișoara Ice Cave allow for a better understanding of the carbon and oxygen isotope fingerprint in carbonates precipitated from freezing of bulk water.

Aragonite is the second most common carbonate cave mineral after calcite. However, in Scărișoara Cave it is not well represented; it is only found in some stalactites, clusterites and cave pearls (Bădău, 1984; Bodolea, 1992). In all of these occurrences, aragonite was identified using polarising microscope observations on thin sections. Aragonite and calcite coexisted as alternating layers in most of the investigated speleothems. All these samples exhibit pseudomorphs of calcite after aragonite (the initial internal structure was changed while the external form was preserved).

Patches of sub-millimetre to millimetre-thick coatings, composed of white, finely crystalline material, were found covering the walls in few sectors within the *Rezervația Mică* (Fig. 14, Stop 3). X-ray diffraction investigations showed these crusts to be composed of **monohydrocalcite**. In addition, when the crusts were stained with alizarin red-S the dark red colour (a darker shade than that obtained when staining calcite or aragonite) confirmed the presence of monohydrocalcite. Crusts composed of monohydrocalcite can only be found in a particular area of the periglacial sector of the cave where the temperature ranges from 0.3 to 3 °C. In this area, monohydrocalcite occurs in a zone where small water droplets hit the ice stalagmite heads, ejecting onto the walls, forming a fine mist (aerosol) environment. Although no water chemistry data is available for this cave passage, the appearance of hydromagnesite and monohydrocalcite speleothems deposited in the same area indicates the likely presence of magnesium-rich solutions (Onac, 2001).

The only explanation we have found for the presence of monohydrocalcite in Scărișoara Cave is the one proposed by Fischbeck (1976) and Fischbeck & Müller (1971). They assumed the following conditions for precipitation of monohydrocalcite: Mg/Ca ratio in solution higher than 1, solution temperature to be lower than 20 °C, and the presence of aerosols. All these conditions are met in Scărișoara Cave. Worldwide, monohydrocalcite has been documented in relatively few caves (Hill & Forti, 1997). In Romania, it has been reported in only two other caves (Humpleu and Lucia Mică; Onac & Ghergari, 1993).

In “Palatul Sânzienelor” (upper part of the “Little Reserve”), patches of white mats of an earthy pasty mass (moonmilk-like speleothems) were collected from a side passage (Fig. 14, Stop 4). The average size of these patches is about 1.5 cm. X-ray diffraction analysis of the samples revealed the presence of **hydromagnesite**. Hydromagnesite is a common carbonate cave mineral, and its presence is not a surprise. However, currently it is the only magnesium carbonate mineral found in Scărișoara. We believe that hydromagnesite was precipitated from magnesium-rich percolating solutions due to the degassing of carbon dioxide in passages located above the periglacial microclimate zone.

Near the monohydrocalcite location, also occur some bright yellow-greenish scaly crusts (Fig. 14, Stop 5; Fig. 18). Under binocular the crystals were translucent and showed adamantine lustre. Chemical analysis of the mineral by energy dispersive secondary X-ray (EDX) shows its composition to be dominated by the elements Pb and Cr, and the remaining being a mixture of Ca, Si, and Al. The X-ray powder diffraction (XRPD) data were collected using a Scintag Pad V diffractometer operated at 45 kV and 40 mA. The instrument employs Cu-K α radiation. The XRPD pattern is sharp and well resolved, indicating a well-crystallised material. The peak search revealed a good match for most of 2-theta values for **crocoite** (PbCrO $_4$), whereas some

of the peaks were assigned to calcite. These values are almost identical to those reported in the ICDD file of crocoite. Refinement of the XRD data using POWDER 2.0 program produced the following monoclinic unit-cell parameters: $a = 7.02$ Å; $b = 7.32$ Å; $c = 6.71$ Å, and $\beta = 102.32^\circ$. Scanning electron microscope images of crocoite show slender prismatic crystals.

Crocoite is a rare mineral even for the surface environment. Its presence in Scărișoara Glacier Cave is enigmatic (Onac, 2001). In the natural environment, the mobile species of chromium is the Cr $^{6+}$ ion. Under oxidising conditions, Cr $^{3+}$ is the stable valence state in equilibrium with the atmosphere, occurring either as the HCrO $_4$ or CrO $_4^{2-}$ anion (Drever, 1997). Because, within the cave environment, the pH is typically in the range of 7 to 8, and the redox potential in the range of +0.4 to +0.6 volts, the Cr $^{3+}$ can not oxidise to form Cr $^{6+}$ (chromate). The precipitation of crocoite in Scărișoara Glacier Cave as a secondary mineral is hard to accept. Considering the remote location of the cave, and the fact that Pb and Cr ions are rare in the environment, a natural origin for this mineral is excluded. Hence, it cannot be considered a true cave mineral. The presence of crocoite raises the question of lead and chromium origin. The only explanation we can put forward is that the occurrence of crocoite has a human-induced origin. It is known that various chromates are used for artificial dye preparation. Thus, dye could have been dumped in the close vicinity of the cave and then crocoite formed when such dye components were transported into the cave by the percolating waters.

The phosphate association from Scărișoara Ice Cave was identified in the lower part of the “Little Reserve” (Fig. 14, Stop 6), where it forms millimetre black-grey dusty crusts, covering both calcite speleothems and limestone boulders on the floor of the cave. The minerals identified by means of XRD are hydroxylapatite, Ca $_5$ (PO $_4$) $_3$ (OH) and brushite, CaHPO $_4$ ·2H $_2$ O. Their presence is related to a small bat colony (Tămaș, 2003).



Fig. 18. Crocoite crusts in *Rezervația Mică*, Scărișoara Ice Cave (photo: B. Onac).

2.6 Gold Museum in Brad

One of world's most amazing collections of native gold samples (most of them recovered from mines in the Metaliferi Mountains, Romania) is exhibited in a unique museum in Brad established around 1896. Over 1000 gold samples and a number of new minerals first discovered and described from Transylvanian gold mines (Au-Ag tellurides) are also exhibited. The museum hosts an interesting collection of archaeological artefacts, extraction and processing mining tools discovered around Brad-Crișcior region. These prove the humans settled here ~5000 years ago and the gold extraction activity has over 2000 years.

2.7 Hunedoara

The city of Hunedoara is located in the eastern foothills of the iron-ore-bearing Poiana Ruscă Mountains, 150 km southwest of Cluj-Napoca. Mentioned since XIIth century as a hub for leather tanning, wool processing and clothing industry, Hunedoara became one of Romania's major metallurgic centers. Iron ores were extracted from nearby area since Dacian and later, in Roman times. During the 14th and 15th centuries the iron foundries and works were famous for their swords and spears.

The Corvins' Castle is one of the best examples of Gothic architecture (later enriched with some Renaissance and Baroque features) in Eastern Central Europe. It was built sometimes before 1400 and later extended by a number of its powerful owners, e.g., Iancu de Hunedoara / János Hunyadi (John of Hunedoara / Hunyad, ~1387–1456), military leader, Governor of Transylvania and by his son, Matei Corvin / Mátyás Hunyadi (Matthias Corvinus, 1443–1490), King of Hungary, in the 15th century. The castle is beautifully preserved, and its interiors host halls with arms and artifacts (<http://www.castelulcorvinilor.ro/corvinscastle/index.php>).

2.8 Cioclovina Cave (Șureanu Mountains)

Cioclovina Cave is one of the most important caves within the Șureanu Mountains (Romania), both in terms of length and scientific interest. It is now well documented that the Cioclovina Cave hosts important archaeological, anthropological, and paleontological remains (Breuil, 1925; Roska, 1925; Banerjee *et al.*, 1999; Păunescu, 2001), along with an impressive collection of rare minerals (Onac, 2003). In order to preserve such a complex scientific archive, the cave was included within the Grădișteța Muncelului – Cioclovina Natural Park.

The Cioclovina Cave is situated in the upper part of the Luncanilor Valley, on the west-southwest side of Șureanu Mountains (Fig. 19, inset). The basic stratigraphy around the Cioclovina Cave consists of a thick carbonate sequence of Upper Jurassic (Stramberk-type facies) and Lower Cretaceous age (Urgonian facies). Underlying the carbonates are gneisses of the Sebeș–Lotru Unit (Getic Nappe), and Permian to Lower

Jurassic (Liassic) detrital deposits (Fig. 19). Cioclovina Cave develops in a 350-m thick sequence of Malm-Neocomian limestones and consists of 1406 m of passages (Tomuș, 1999).

The minerals observed during this field trip, however, are located in various outcrops scattered along the main gallery (~450 m) in the vicinity of both the natural and artificial entrances in the Cioclovina Uscată (Dry Cioclovina) Cave (Fig. 20). In this section the relative humidity is between 65 and 85%, while the temperature remains constant year-round in the range of 8–9 °C.

Although the cave has a natural entrance, this one is rarely used. A mining gallery dug during the guano-phosphate exploitation is now the preferred entrance. *The cave is gated and the access is absolutely restricted unless a special permission from the Commission of Natural Monuments of the Romanian Academy and from the Grădișteța Muncelului – Cioclovina Natural Park Administration is obtained in advance.*

The cave has been known since the late 19th century when scientists visited it to search for cave bear fossils and to investigate the extensive phosphate deposit. Much of the 15 to 20 m thick phosphate deposit was mined out of the cave between 1912 and 1941 (Breban *et al.*, 2003). Nevertheless, in many parts of the cave one can still observe layers of phosphate sediments (5 to 6 m in thickness) covered by flowstone in their upper part.

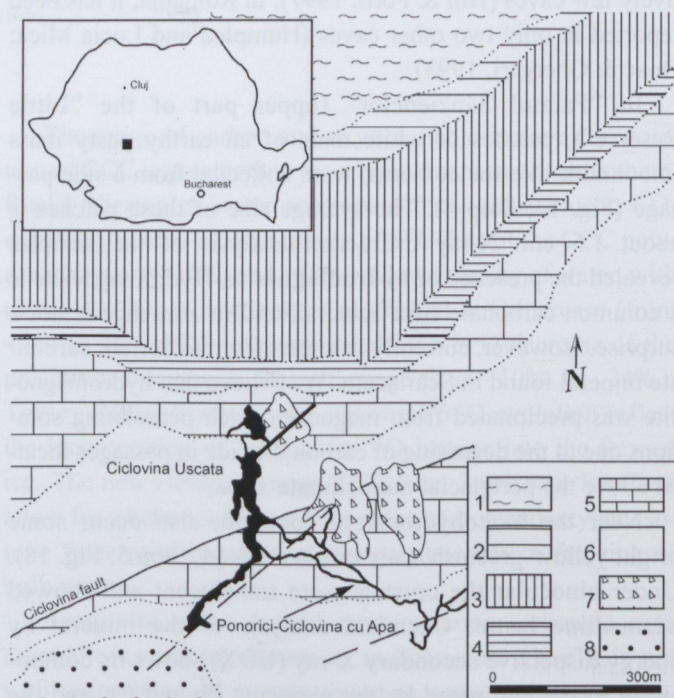


Fig. 19. Location of the Cioclovina cave system and its surrounding geology. 1 – micaschists and gneiss (Precambrian); 2 – conglomerates and red sandstones (Permian); 3 – conglomerates and sandstones with schistose intercalations (Liassic); 4 – carbonate sandstones (Dogger); 5 – limestone with chert intercalations (Oxfordian–Tithonic); 6 – reef limestone; 7 – brecciated limestone; 8 – sandstones and clays (Cenomanian); Cioclovina Uscată and the underlying Ponori-Cioclovina cu Apă cave system are in black (after Stilla, 1981, modified).

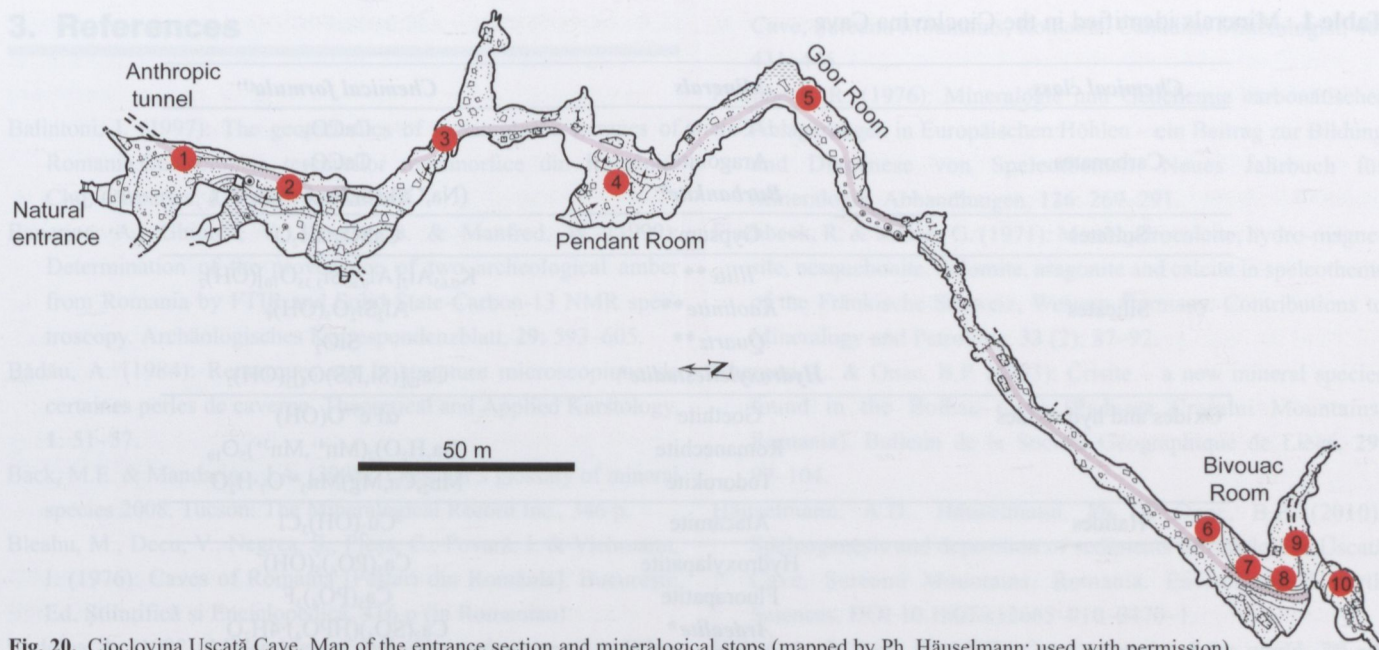


Fig. 20. Cioclovina Uscată Cave. Map of the entrance section and mineralogical stops (mapped by Ph. Häuselmann; used with permission).

A major consequence of mining out the phosphate-rich sediments is that several good exposures are now available throughout the lower part of the cave. The clastic sediments, exposed between the cave entrance and the middle part of the Bivouac Room are typical alluvial deposits of a variety of grain sizes (Häuselmann *et al.*, 2010; Fig. 21). Phosphate-rich solutions percolated the sediment column and under various pH conditions reacted and phosphatized to various degrees the sediment (Fig. 22). In a restricted section of the Bivouac Room the overburden sediment was significant and the underlying material has been heavily compacted so that textures and structures of the original sediments cannot longer be recognised. In this part of the cave, owing to microbial processes, the temperature inside the buried guano increased until spontaneous ignition led to its combustion,

converting the sediment to a dark brown colour. This thermal process further obliterated the outlines of the original depositional features and caused the formation of some high-temperature minerals (berlinite, hydroxyllestadite; Onac & White, 2003; Onac & Effenberger, 2007; Onac *et al.*, 2006a).

The phosphate deposit located within the Cioclovina Uscată (Dry Cioclovina) Cave contains a fascinating assemblage of minerals that includes, apart from many rare phosphates, several carbonates, silicates, sulfates and hydroxide species (see Table 1). Most of the minerals identified within the phosphate deposit form nodules, crusts, bands of earthy masses interbedded with sand, gravel, clay and concentric layers around weathered limestone blocks, volcanic, and metamorphic chunks. Only a few of the minerals form euhedral or



Fig. 21. Phosphate-rich sediments in Cioclovina Cave (photo: B. Onac).



Fig. 22. Highly phosphatized limestone blocks and sediments (Bivouac Room; photo: B. Onac).

Table 1. Minerals identified in the Cioclovina Cave.

| Chemical class | Minerals | Chemical formula ⁽¹⁾ |
|-----------------------|------------------------------|--|
| Carbonates | Calcite | CaCO ₃ |
| | Aragonite | CaCO ₃ |
| | Burbankite* | (Na,Ca) ₃ (Sr,Ba,Ce) ₃ (CO ₃) ₅ |
| Sulfates | Gypsum | CaSO ₄ ·2H ₂ O |
| Silicates | <i>Illite**</i> | K _{0.65} Al ₂ [Al _{0.65} Si _{3.35} O ₁₀](OH) ₂ |
| | <i>Kaolinite**</i> | Al ₂ Si ₂ O ₅ (OH) ₄ |
| | <i>Quartz**</i> | SiO ₂ |
| | Hydroxyllellestadite* | Ca ₁₀ [(Si,P,S)O ₄] ₃ (OH) ₂ |
| Oxides and hydroxides | Goethite | αFe ³⁺ O(OH) |
| | Romanechite | (Ba,H ₂ O) ₂ (Mn ⁴⁺ ,Mn ³⁺) ₅ O ₁₀ |
| | Todorokite | Mn ₂ ,Ca,MgMn ₃ ⁴⁺ O ₇ ·H ₂ O |
| Halides | Atacamite | Cu ₂ (OH) ₃ Cl |
| Phosphates | Hydroxylapatite | Ca ₅ (PO ₄) ₃ (OH) |
| | Fluorapatite | Ca ₅ (PO ₄) ₃ F |
| | Ardealite* | Ca ₂ (SO ₄)(HPO ₄)·4H ₂ O |
| | Berlinite* | AlPO ₄ |
| | Brushite | CaHPO ₄ ·2H ₂ O |
| | Churchite-(Y)* | YPO ₄ ·2H ₂ O |
| | Collinsite | Ca ₂ (Mg,Fe ²⁺)(PO ₄) ₂ ·2H ₂ O |
| | Crandallite | CaAl ₃ (PO ₄) ₂ (OH) ₅ ·H ₂ O |
| | Foggite* | CaAl(PO ₄)(OH) ₂ ·H ₂ O |
| | Leucophosphate | KFe ₂ ³⁺ (PO ₄) ₂ (OH)·2H ₂ O |
| | Monetite | CaHPO ₄ |
| | Sampleite | NaCaCu ₅ ²⁺ (PO ₄) ₄ Cl·5H ₂ O |
| | Taranakite | K ₃ (Al,Fe) ₅ (HPO ₄) ₆ (PO ₄) ₂ ·18H ₂ O |
| | Variscite | AlPO ₄ ·2H ₂ O |

⁽¹⁾ According to Back & Mandarino (2008) & Pasero *et al.* (2010)

* First documented in a cave environment worldwide (**bold italics**)

** Not secondary cave mineral (*italics*)

subhedral crystals; all the others appear as earthy masses (Constantinescu *et al.*, 1999; Dumitraş & Marincea, 2000; Dumitraş *et al.*, 2004, 2008; Marincea & Dumitraş, 2003, 2005; Marincea *et al.*, 2002; Onac & White, 2003; Onac & Effenberger, 2007; Onac *et al.*, 2002, 2004, 2005, 2006a, 2006b, 2007, 2009). We plan to have 9 stops within the cave (Fig. 20). At each of these stops we will discuss the mineral assemblages and their genesis.

A human skull was recovered from the phosphate deposit in 1941 but dated only recently by means of ¹⁴C AMS to 29,000±700 yrs BP (Olariu *et al.*, 2002). The skull belongs to a *Homo sapiens fossilis* that inhabited the cave in the Upper Paleolithic time (Aurignacian archaeological period).

2.9 Turda Salt Mine

The city of Turda hosts one of the most important salt mines in Transylvania. Although it was known since ancient times, salt mining activities only begun during the Roman period. In

the Middle Ages, Turda was one of the largest salt extraction places in the entire southeastern Europe. No mechanical equipment was used to extract salt (only human and horse-power) until very recently. The salt was extracted using the classic room mining method with bell-shaped chambers. From the 1850s chambers of trapezoidal cross-section were used and a new haulage adit was begun in 1853, which finally reached 917 m in length (850 m is still accessible). Salt mining ended here in 1932. The chambers were used as anti-air craft shelters during the World War II. The former salt mine was later adapted for the purposes of tourism and therapeutics. The temperature in the salt mine remains constant (11–12 °C) year around, whereas the relative humidity reaches 80% (Racoviţă & Petrescu, 1992). Due to its long tunnels, large galleries, impressive bell-shaped chambers carved only with hammer and chisel, along with its great acoustics and very healthy microclimate, Turda Salt Mine is an excellent destination for anyone passing by. More information can be found at http://romania.ici.ro/en/turism/c_salinatorurda.html

3. References

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Appendix – Itinerary for IMA2010 RO4 Field trip

Saturday, August 14, 2010 (Day 0): Arrival of participants for the RO4 Cave minerals of Romania field trip

Sunday, August 15, 2010 (Day 1)

- 08.30–09.00 Meeting in front of the Babeş–Bolyai University (Kogălniceanu st. 1, Cluj-Napoca)
- 09.00–11.30 Travel to Şuncuiuş
- 11.30–12.30 Lunch at the entrance in Vântului Cave
- 12.30–15.30 Visit of Vântului Cave
- 15.30–15.45 Travel to Bolhac Cave
- 15.45–16.45 Visit of Bolhac Cave
- 16.45–19.00 Travel to Chişcău via Bratca–Beiuş
- 19.00–21.00 Accommodation and dinner at Mance Guest House in Chişcău

Monday, August 16, 2010 (Day 2)

- 07.30–08.15 Breakfast at Mance Guest House
- 08.15–08.30 Travel to Urşilor Cave at Chişcău
- 08.30–10.30 Visit of Urşilor Cave
- 10.30–12.00 Travel to Vârtoş
- 12.00–13.30 Lunch at Mont Blanc Guest House
- 13.30–14.00 Travel to Gârda de Sus
- 14.00–16.00 Hike to the Scărişoara Guest House (6 km on a mild slope)
- 15.30–16.00 Break time
- 16.00–16.30 Hike to the Scărişoara Ice Cave (1 km on a mild slope)
- 16.30–19.30 Visit of Scărişoara Ice Cave (temperature is around freezing point; warm clothes and vertical gear [rope climbing equipment] needed)
- 19.30–20.00 Hike back to the Scărişoara Guest House
- 20.00–21.30 Dinner at Scărişoara Guest House

Tuesday, August 17, 2010 (Day 3)

- 07.45–08.30 Breakfast at Scărişoara Guest House
- 08.30–09.30 Hike downhill to Gârda de Sus

- 09.30–11.30 Travel to Brad
- 11.30–13.00 Visit of Gold Museum in Brad
- 13.00–14.00 Lunch in a local restaurant
- 14.00–16.30 Travel to Hunedoara
- 16.30–18.00 Visit of Corvins' Castle
- 18.00–19.00 Travel to Băcia for dinner and accommodation at Casablanca Motel

Wednesday, August 18, 2010 (Day 4)

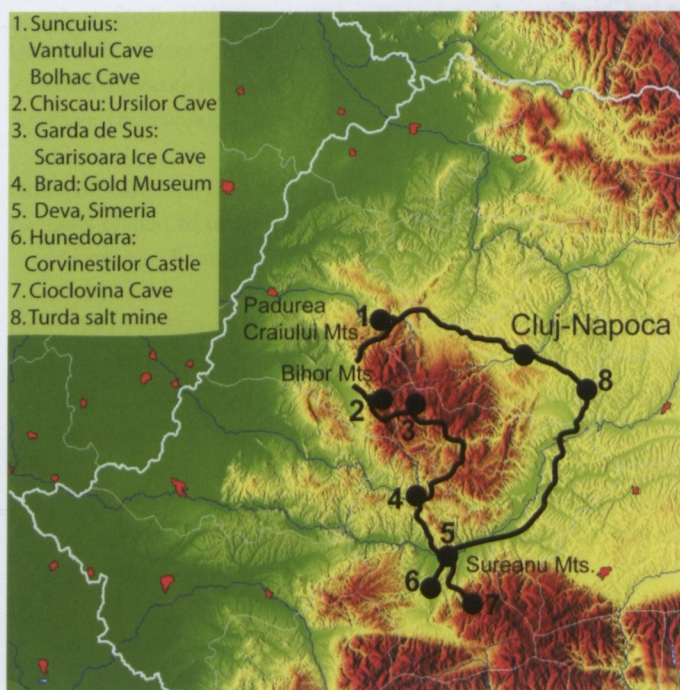
- 07.45–08.30 Breakfast
- 08.30–11.30 Travel to Cioclovina Cave (includes 1 km hike on a mild slope)
- 11.30–12.30 Lunch in the field
- 12.30–16.30 Visit of Cioclovina Cave
- 16.30–19.30 Return to Băcia (dinner and accommodation)

Thursday, August 19, 2010 (Day 5)

- 08.00–09.00 Breakfast
- 09.00–14.00 Travel to Turda (lunch) and visit of the Turda Salt Mine
- 14.00–15.00 Travel to Cluj-Napoca
- 15.00–20.00 Visit of Cluj-Napoca and farewell dinner
- 20.00–24.00 Departure for Budapest (optional)

Friday, August 20, 2010

- 06.00–12.00 Departure of participants towards IMA 2010 in Budapest



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USEFUL NOTES

ures and tables), notes (Figures and tables), and short communications. Manuscripts should be submitted as a single file in PDF format. Authors are asked to submit their manuscripts in a format that is compatible with the software used to create them. Manuscripts should be submitted in a format that is compatible with the software used to create them. Manuscripts should be submitted in a format that is compatible with the software used to create them.

Articles longer than 10,000 words should be submitted in two parts. The first part should be submitted in a format that is compatible with the software used to create them. The second part should be submitted in a format that is compatible with the software used to create them. The first part should be submitted in a format that is compatible with the software used to create them. The second part should be submitted in a format that is compatible with the software used to create them.

Higher priority may be given to manuscripts that are submitted in a format that is compatible with the software used to create them. Manuscripts should be submitted in a format that is compatible with the software used to create them. Manuscripts should be submitted in a format that is compatible with the software used to create them. Manuscripts should be submitted in a format that is compatible with the software used to create them.

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LANGUAGE

The language of the manuscript should be English.

PREPARATION OF THE MANUSCRIPT

The title has to be short and informative. The title should be short and informative. The title should be short and informative. The title should be short and informative. The title should be short and informative. The title should be short and informative. The title should be short and informative. The title should be short and informative.

The front page has to carry the title, the authors' names, and the address(es) of the author(s). The front page has to carry the title, the authors' names, and the address(es) of the author(s). The front page has to carry the title, the authors' names, and the address(es) of the author(s). The front page has to carry the title, the authors' names, and the address(es) of the author(s).

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Figures and tables

Figures and tables should be submitted in a format that is compatible with the software used to create them. Figures and tables should be submitted in a format that is compatible with the software used to create them. Figures and tables should be submitted in a format that is compatible with the software used to create them. Figures and tables should be submitted in a format that is compatible with the software used to create them.

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References and Methods - References

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The reference list can only consist of published papers, M.Sc., Ph.D., and D.Sc. theses, and papers in press. Only works cited previously in the text can be put in the reference list.

Best, M.G., Christensen, E.H. (eds.) (2001). *Igneous petrology*. Blackwell, Edinburgh, 938p.

Edwards, C.B., and others (1997). *Microthermometric and Raman spectroscopic characterization of CO₂ in fluid inclusions and the*. Edinburgh, 447-472.

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EGY-26

14.00-16.30 Travel to Pisa/Porto

18.00-19.00 Travel to hotel for dinner and accommodation at Castillan Hotel

08:30-11:30 Travel to Chichén Itzá (approx. 1 km bike in a 19th century)

12.30-16.30 Visit of Chichén Itzá

Thursday, August 19, 2010 (Day 5)

08:00-09:00 Breakfast

14.00-15.00 Travel to Chi-Nan

20.00-24.00 Departure for Budapest (overnight)

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INSTRUCTIONS FOR AUTHORS

GENERAL

Acta Mineralogica-Petrographica (AMP) publishes articles (papers longer than 4 printed pages but shorter than 16 pages, including figures and tables), notes (not longer than 4 pages, including figures and tables), and short communications (book reviews, short scientific notices, current research projects, comments on formerly published papers, and necrologies of 1 printed page) dealing with crystallography, mineralogy, ore deposits, petrology, volcanology, geochemistry and other applied topics related to the environment and archaeometry. Articles longer than the given extent can be published only with the prior agreement of the editorial board.

In the form of two subseries, AMP publishes materials of conferences (AMP Abstract Series) and field guides (AMP Field Guide Series), or, occasionally supplement issues related to other scientific events.

The journal accepts papers that represent new and original scientific results, which have not appeared elsewhere before, and are not in press either.

All articles and notes submitted to AMP are reviewed by two referees (short communications will be reviewed only by one referee) and are normally published in the order of acceptance, however, higher priority may be given to Hungarian researches and results coming from the Alpine-Carpathian-Dinaric region. Of course, the editorial board does accept papers dealing with other regions as well, let they be compiled either by Hungarian or foreign authors.

The manuscripts (prepared in harmony of the instructions below) must be submitted to the Editorial Office in triplicate. All pages must carry the author's name, and must be numbered. At this stage (revision), original illustrations and photographs are not required, though, quality copies are needed. It is favourable, if printable manuscripts are sent on disk, as well. In these cases the use of Microsoft Word or any other IBM compatible editing programmes is suggested.

LANGUAGE

The language of AMP is English.

PREPARATION OF THE MANUSCRIPT

The different parts of the manuscript need to meet the instructions below:

Title

The title has to be short and informative. No subtitles if possible. If the main title is too long, an additional shortened title is needed for the running head.

Author

The front page has to carry (under the main title) the full name(s) (forename, surname), affiliation(s), current address(es), e-mail address(es) of the author(s).

Abstract and keywords

The abstract is required to be brief (max. 250 words), and has to highlight the aims and the results of the article. The abstracts of notes are alike (but max. 120 words). As far as possible, citations have to be avoided.

The abstract has to be followed by 4 to 10 keywords.

Text and citations

The format of the manuscripts is required to be: double-spacing (same for the abstract), text only on one side of the page, size 12 Times New Roman fonts. Margin width is 2.5 cm, except the left margin, which has to be 3.5 cm wide. Underlines and highlights ought not be used. Please avoid the use of foot and end notes. Accents of Romanian, Slovakian, Czech, Croatian etc. characters must be marked on the manuscript clearly.

When compiling the paper an Introduction – Geological setting – Materials and Methods – Results – Conclusions structure is suggested.

The form of citations is: the author's surname followed by the date of publication e.g. (Szederkényi, 1996). In case of two authors: (Rosso and Bodnar, 1995) If there are more than two authors, after the first name the co-authors must be denoted as "et al.", e.g. (Roser et al., 1980).

REFERENCES

The reference list can only consist of published papers, M.Sc., Ph.D. and D.Sc. theses, and papers in press.

Only works cited previously in the text can be put in the reference list. Examples:

Best, M.G., Christiansen, E.H. (eds.) (2001): Igneous petrology. Blackwell, Edinburgh, 458p.

Upton, B.G.J., Emeleus, C.H. (1987): Mid-Proterozoic alkaline magmatism in southern Greenland: the Gardar province. In: Fitton, J.G., Upton, B.G.J. (eds.): Alkaline Igneous Rocks. Blackwell, Edinburgh, 449–472.

Rosso, K.M., Bodnar, R.J. (1995): Microthermometric and Raman spectroscopic detection limits of CO₂ in fluid inclusions and the Raman spectroscopic characterization of CO₂. *Geochimica et Cosmochimica Acta*, **59**, 3961–3975.

Szederkényi, T. (1996): Metamorphic formations and their correlation in the Hungarian part of Tisia Megaunit (Tisia Megaunit Terrane). *Acta Mineralogica-Petrographica*, **37**, 143–160.

Bakker, R.J. (2002): <http://www.unileoben.ac.at/~buero62/minpet/Ronald/Programs/Computer.html>. Accessed: June 15, 2003.

The full titles of journals ought to be given. In case more works of the same author are published in the same year, then these has to be differentiated by using a, b, etc. after the date.

ILLUSTRATIONS

Finally, each figure, map, photograph, drawing, table has to be attached in three copies, they must be numbered and carry the name of the author on their reverse. All the illustrations ought to be printed on separate sheets, captions as well if possible. Foldout tables and maps are not accepted. In case an illustration is not presented in digital form then one of the copies has to be submitted as glossy photographic print suitable for direct reproduction. Photographs must be clear and sharp. The other two copies of the illustrations can be quality reproductions. Coloured figure, map or photograph can only be published at the expense of the author(s).

The width of the illustrations can be 56, 87, 118, or 180 mm. The maximum height is 240 mm (with caption).

All figures, maps, photographs and tables are placed in the text, hence, it is favourable if in case of whole page illustrations enough space is left on the bottom for inserting captions. In the final form the size of the fonts on the illustrations must be at least 1,5 mm, their outline must be 0,1 mm wide. Digital documents should be submitted in JPG-format. The resolution of line-drawings must be 400 dpi, while that of photographs must be 600 dpi. The use of Corel Draw for preparing figures is highly appreciated, and in this case please submit the .CDR file, as well.

PROOFS AND OFFPRINTS

After revision the author(s) receive only the page-proof. The accepted and revised manuscripts need to be returned to the Editors either on disc, CD or as an e-mail attachment. Proofreading must be limited to the correction of typographical errors. If an illustration cannot be presented in digital form, it must be submitted as a high quality camera-ready print.

The author(s) will receive 25 free offprints. On payment of the full price, further offprints can be ordered when the corrected proofs are sent back.

Manuscripts for publication in the AMP should be submitted to:

Dr. Pál Molnár Elemér

E-mail: palm@geo.u-szeged.hu

Dr. Batki Anikó

E-mail: batki@geo.u-szeged.hu

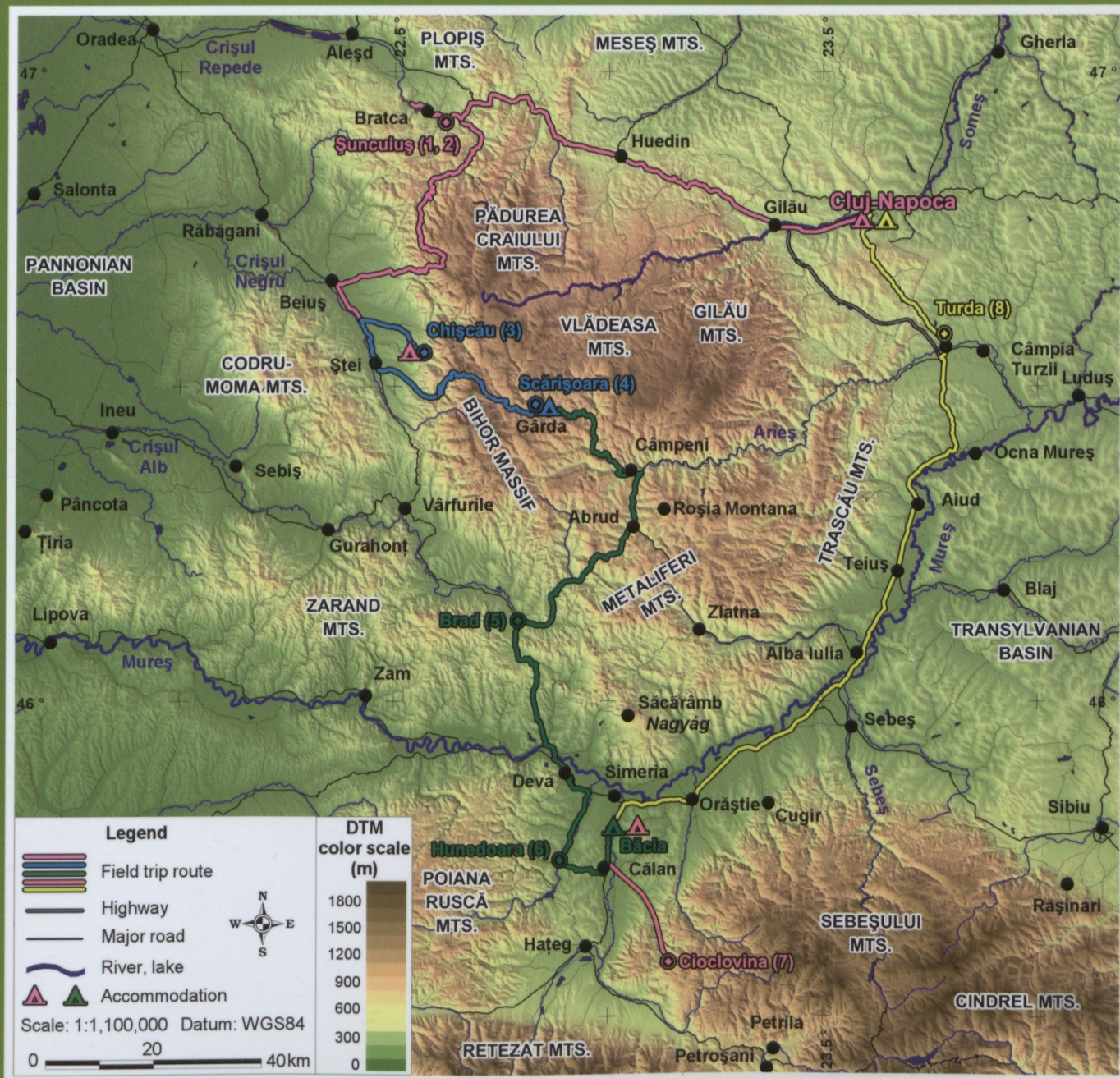
Phone: 00-36-62-544-683, Fax: 00-36-62-426-479

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H-6701 Szeged, Hungary

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MAP OF THE IMA2010 FIELD TRIP R04



Map provided by the Stockwork Exploration Ltd. (www.stockwork.eu)